Changes in Water Absorption and Swollen Volume in Extruded Alkaline Peroxide Pretreated Rice Hulls

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ABSTRACT

Rice hulls were pretreated with an alkaline (pH 11.5) solution of hydrogen peroxide (1%) and then extruded. Pretreatment of rice hulls (4% db) at 50ºC for 12 hr promoted 94.4% silica reduction, caused lignin solubilization and increased water absorption index (54%) and swollen volume (44%). The effects of temperature (125, 175, and 225ºC), moisture content (25, 30, and 35%) and screw speed (120, 140, and 160 rpm) on water absorption and swollen volume of rice hulls fiber were evaluated after extrusion in a single-screw extruder. Operational conditions that produced the most modified product with regard to the functional properties were: 125°C, 35% moisture, and 120 rpm. Extruded fiber had a water absorption index 95% higher and swollen volume 138% higher than the unprocessed material. Microscopic examination showed a slight effect on the hulls epidermis after pretreatment, while extrusion promoted cellular structure disruption.

Interest in fiber consumption in the daily diet has increased lately, and production of baked products containing bran or other types of fiber-rich fraction of cereals has increased. Most studies showed that fiber addition had negative effects on the products, including decreased final baked volume and gritty texture (Dougherty et al 1988, Gould et al 1989). These deleterious effects could be minimized if fibers were modified to have a softer texture and increased water absorbency and swelling characteristics (Jasberg et al 1989a,b).

Gould (1984), Gould et al (1989), and Jasberg et al (1989a,b) modified lignocellulosic materials using an alkaline hydrogen peroxide solution to solubilize a portion of the original lignin, obtaining a product with increased water absorption capacity that, on microscopic examination, had a more open structure when compared to the original fiber.

Among physical treatments, extrusion has been suggested as efficient for improving fiber functionality. Artz et al (1990a,b) studied the effect of extrusion on corn bran and corn starch blends and found that there was no major change in the corn bran fiber. They suggested that it would be advantageous to study the modification of fiber extruded by itself and recommended application of either chemical or enzymatic pretreatment.

Rice hulls are rich in fiber and have relatively low starch and protein content, but their use in feed or food is hindered by a high silica content, which can be removed by alkaline solutions (Houston 1972). Therefore, we studied the effects of alkaline hydrogen peroxide pretreatment and extrusion cooking to modify water absorption and swollen volume of rice hulls fibers.

MATERIALS AND METHODS

Materials

Rice hulls were furnished by a local (Londrina, PR) rice milling plant. All chemicals were reagent grade.

Alkaline Pretreatment

Milled rice hulls (0.42–1.2 mm particle size) were treated with alkaline hydrogen peroxide (0.1%, pH 11.5), as described in Gould (1984), using 4% hulls (w/v), 50°C, and 12-hr reaction time, with periodic shaking. After neutralization with 5*N* HCl, the material was collected by filtration, washed with water, and dried in a forced air-oven at 55°C for 24 hr (Larrea et al 1994).

After drying, the treated material was ground in a pin mill (14,000 rpm, model 160Z, Alpine, Augsburg, Germany) fitted with a 1.0-mm screen. Only material with particle size in the 0.21–0.42 mm range was used for water absorption index and swollen volume determination.

Extrusion

For each run, pretreated material was conditioned to the desired moisture content, according to the experimental design. Material was placed in sealed polyethylene bags and allowed to equilibrate for 16 hr at 10°C and then extruded in a single-screw extruder (Cerealtec CT-L15, Campinas, Brazil). The extruder has a barrel 420 mm in length, 19.4 mm in diameter, three zone and die assembly electric heaters, 2:1 compression ratio screw, and 9 mm die diameter. Processing temperature in zone 1 was kept constant at 85°C. The temperature of zones 2, 3, and die were the same and varied with experimental design.

The extruder was operated at steady state for each set of conditions. Attainment of steady state was judged by a constant amperage. Samples (200 g, wb) were then collected, dried at 80°C in a forced-air convection oven to 13% moisture, coarsely ground (Tecnal mill, São Paulo, Brazil) and finely ground in the Alpine mill. To determine water absorption and swollen volume, material with particle size in the 0.21–0.42 mm range was used.

Analytical Methods

Moisture (44-15A), protein (46-13), ash (08-01) and lipids (10-30) were determined according to AACC approved methods (AACC 1995). Silica was estimated according to method 3.005 of the AOAC (1984).

Cellulose, hemicellulose, and lignin were determined as in Bailey (1967). Water absorption and swollen volume were determined using the methods described by Gould et al (1989). All determinations were run in triplicate

Electron Microscopy and X-ray Diffractometry

Scanning electron micrographs were obtained using a JEOL T-300 microscope with 10 and 20 Kv acceleration. Samples were dried over silica gel at 35°C, during 10 days to eliminate residual moisture, coated with gold in high vacuum, and examined in the microscope. X-ray diffractometry of samples was obtained with a Freiberg Prazisionsmechanic unit (model VRD-6, Germany). Set-

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tings were 40 kv, 20 mA, 0.02° step sampling, 5-sec detection time. Crystallinity index was estimated as the ratio between crystalline area and total area.

Experimental Design for Extrusion

An incomplete factorial design of the surface response methodology was employed, with three independent variables at three levels of variation (Box and Behnken 1960). The independent variables were: extruder temperature (125, 175, and 225°C), moisture content (25, 30, and 35%), and screw speed (120, 140, and 160 rpm). Dependent variables were water absorption and swollen volume. Experimental data were analyzed using the Statistical Analysis System (SAS 1985) to fit second order polynomial equations to response variables. Three-dimensional contour plots were generated from the fitted models, using the Statistica (Statsoft, Oklahoma) computer software.

RESULTS AND DISCUSSION

Rice Hulls Composition

The major modification in rice hulls composition after pretreatment with alkaline hydrogen peroxide was a decrease in ash from 15.73 to 1.39%, due to removal of 94.4% of the silica (Table I). Reaction with sodium hydroxide in the pretreatment resulted in soluble silicates, that were eliminated during the washing procedure (Houston 1972).

A reduction in protein and lipid concentration occurred. Soluble proteins and saponified fatty acids (due to the alkaline pH) (Nawar 1985) were probably lost during washing (Chen and Houston 1970). Minor causes, like fatty acid oxidation by oxidryl and superoxide radicals formed during decomposition of hydrogen peroxide should be also considered (Jacks and Hensarling 1989). Total fiber and nonnitrogenous material showed relative increases that could be attributed to the decrease of other components.

Functional Properties of Treated Rice Hulls

After pretreatment, water absorption increased 57% and swollen volume increased 44% (Table II). These increased values may be the result of removal of silica and lignin solubilization and elimination (Table III). Houston (1972) described rice hulls as containing a resistant structure formed by lignin and silica. The destruction of this rigid structure could increase the size of interstitial spaces within the cell wall material and facilitate the hydration of cell wall components.

According to various authors (Gould 1984, Gould et al 1989, Jasberg et al 1989a), alkaline hydrogen peroxide removed lignin by solubilization, while at the same time modifying cellulose crystallinity and increasing water absorption. Ning et al (1991) stated that the modification of water absorption capacity may be partially due to the swelling of the physical structure of the fiber by alkali. According to Table III, there was a increase in the cellulose content of the fiber but it can be a relative increase, caused by the reduction of other components.

Effect of Extrusion on Functional Properties

The results for water absorption and swollen volume of the extruded rice hulls were used to develop regression models (Table IV). Correlation coefficients >80% and coefficients of variation <10% indicate good agreement between experimental data and models (Joglekar and May 1987). According to the analysis of variance, water absorption was affected by linear effects of temperature and moisture content of the feed material. Swollen volume was affected only by the linear effect of temperature.

Effect of screw speed was not significant for the two studied responses. Probably, the differences in residence times of the material within the extruder due to the various levels of screw speed applied were not so great as to promote substantial differences in the fiber properties.

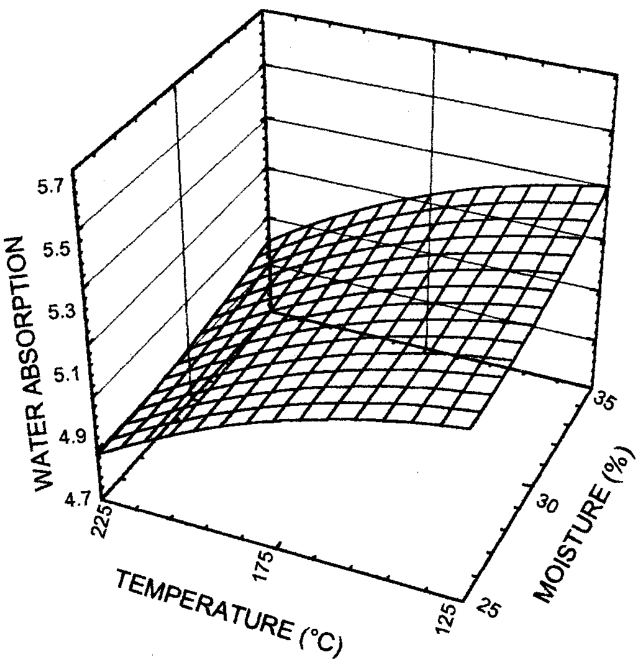

Fig. 1. Effect of extrusion conditions on water absorption index of rice hulls (screw speed = 120 rpm).

TABLE I
Chemical Composition (%, dwb) of Raw and Alkaline Treated Rice Hulls

	Rice Hulls	
Components	**Raw**	**Pretreated**
Protein[a]	3.32a[b]	1.57b
Lipids	0.72a	0.33b
Fiber		
Cellulose	32.28b	45.37a
Hemicellulose	27.02a	28.94a
Lignin	20.67a	19.15a
Ash (without silica)	0.80a	0.56b
Silica	14.93a	0.83b
Nitrogen-free extract[c]	0.26b	3.25a

[a] N × 5.95.
[b] Means in the same row followed by the same letter are not significantly different at the 5% level (Tukey's test).
[c] By difference.

TABLE II
Functional Properties of Raw and Alkaline Treated Rice Hulls

	Rice Hulls	
Properties	**Raw**	**Pretreated**
Water absorption (g/g of dry material)	2.86b[a]	4.40a
Swollen volume (mL/g of dry material)	5.2b	7.5a

[a] Means followed by the same letter within a row are not significantly different at the 5% level.

TABLE III
Composition (%, dwb) of Fiber in Raw and Alkaline Treated Rice Hulls

	Rice Fiber	
Components	**Raw**	**Pretreated**
Cellulose	39.48b[a]	46.01a
Hemicellulose	32.05a	29.35a
Lignin	25.70a	19.42b

[a] Means followed by the same letter within a row are not significantly different at the 5% level.

Surface plots obtained from the mathematical models, with screw speed fixed at 120 rpm (nonsignificant variable), are shown in Figures 1 and 2. Under all the operational conditions of extrusion, water absorption and swollen volume were higher than in pretreated hulls. This is an indication that extrusion promoted fiber structure modification allowing water penetration and retention. Water absorption increased as lower temperature and higher moisture content were used, or when extrusion conditions were less harsh. Swollen volume also increased with lower extrusion temperature.

On the other hand, when shearing increased, either by reducing moisture content or by increasing temperature, the values of the two functional properties decreased. Probably, in these experimental conditions, an excessive structural disruption occurred, destroying the porous cell wall conformation. Gould et al (1989) reported a similar effect caused by pressing or ball milling of fiber, that would destroy the open internal structure. Ning et al (1991) observed similar effect after extrusion of corn fiber with alkaline or acid pretreatment.

Overlapped contour plots of the response variables (Fig. 3), showed the experimental region where both water absorption and swollen volume reached maximum values (shaded area). Opera-

TABLE IV
Regression Equation Coefficients[a] for Water Absorption Index and Swollen Volume

	Water Absorption Index	Swollen Volume
Intercept	5.12	10.13
Temperature	–0.24**	–0.95*
Moisture	0.21*	0.53
Screw speed	0.03	–0.08
Temperature × temperature	–0.08	0.61
Moisture × moisture	0.03	0.26
Speed × speed.	–0.06	0.06
Temperature × moisture	–0.01	0.20
Temperature × speed	0.00	0.50
Moisture × speed	0.14	0.25
R^2	0.87	0.81

[a] *,** = significant at $P < 0,05$ and $P < 0,01$, respectively.

TABLE V
Crystalinity Index of Rice Hulls Cellulose

Rice Hulls	Crystallinity Index[a] (%)
Raw	35
Pretreated	34
Pretreated and extruded	33

[a] Crystalline area/total area, as determined by X-ray diffractometry.

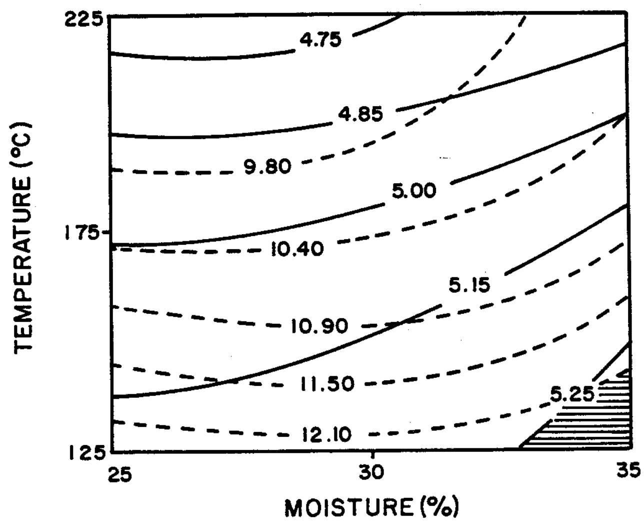

Fig. 3. Conditions (shaded area) for rice hulls extrusion to increase water absorption and swollen volume (screw speed = 120 rpm).

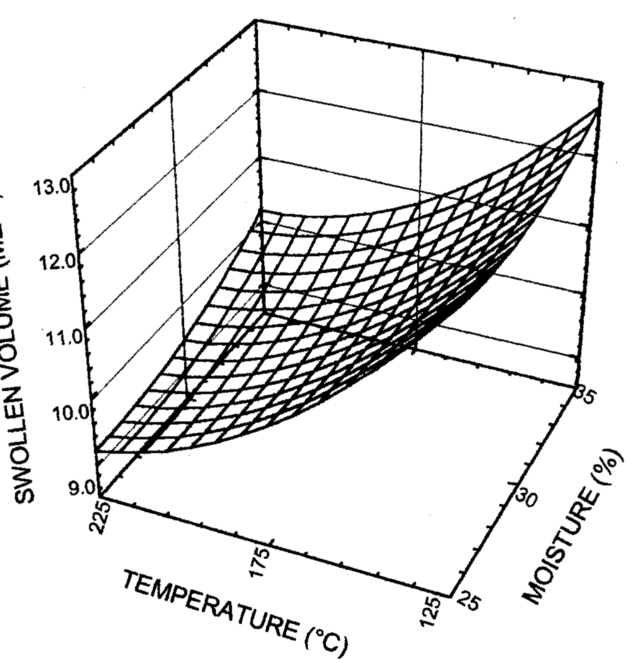

Fig. 2. Effect of extrusion conditions on swollen volume of rice hulls (screw speed = 120 rpm).

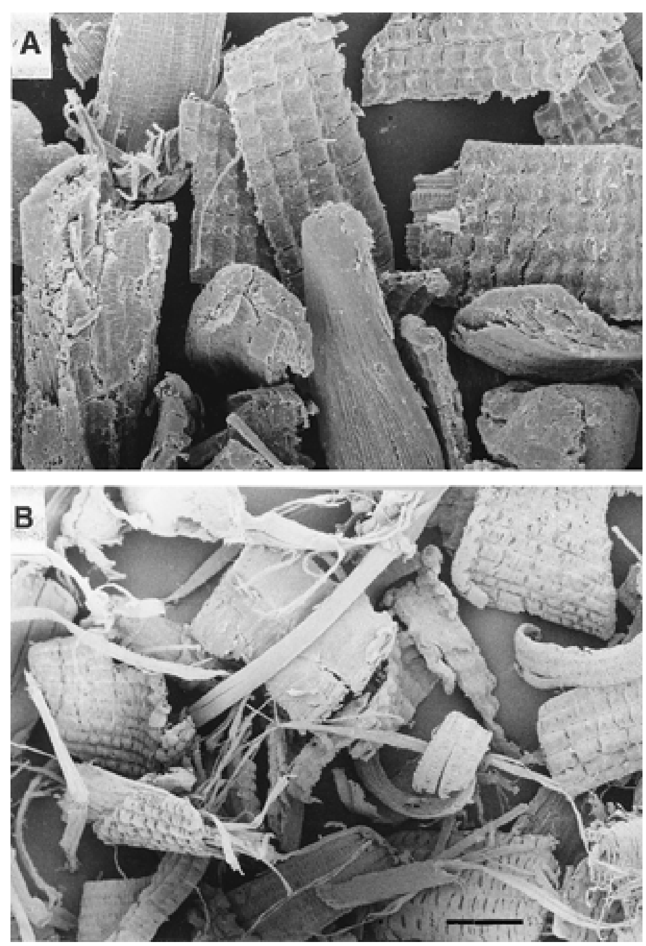

Fig. 4. Scanning electron micrographs of rice hulls: **A** pretreated, **B** pretreated and extruded at 125ºC, 35% moisture, and 140 rpm (bar = 10 µm).

tional conditions recommended to obtain the most modified material were defined as: 125°C, 35% moisture content, and 120 rpm screw speed, when water absorption was 5.3 g of H_2O/g of dry matter and swollen volume was 12.4 mL/g of dry matter. Extrusion improved functional properties of rice hulls by 24% for water absorption and by 65% for swollen volume, in relation to the pretreated material. When compared to the untreated material, the improvement was 95% for water absorption and 138% for swollen volume.

To investigate the operational area with temperature <125°C and moisture >35% could be interesting. However, it was impossible due to extruder limitations, because the screw does not turn with this type of material at this low temperature, and water is partially pressed out at higher moisture content.

Figure 4a is a micrograph of the rice hulls after pretreatment. The external epidermis was well organized but showed fissures between cells formed by silica removal and partial delignification. Internal epidermis did not show signs of modification, but protective cuticula was fragmented, which could facilitate water absorption and fiber swelling. Figure 4b of the extruded product showed further disruption of the fiber structure as increased porosity and reduced particle size. This structure, more open than the pretreated material, could facilitate water penetration and absorption, improving functionality related with these properties. Results of X-ray crystallography suggested that there were only minor changes in cellulose crystalline structure promoted by pretreatment or extrusion (Table V). No significant changes in the X-ray diffraction pattern were observed, only the ratio of crystalline area and total area of the spectra decreased slightly when compared with those of the raw fiber.

CONCLUSION

The main advantage of using rice hulls was the possibility of studying the effect of the treatments in a fiber-rich material with little interference from other food components. Cellulose crystallinity appeared to be only slightly affected by pretreatment or extrusion. Most of the modification in water absorbency was achieved in the pretreatment and silica removal was probably the major factor responsible for the porous and fragile structure formed. High temperature and low moisture during harsh extrusion conditions resulted in less porous material, with lower water absorption capacity and swollen volume. Pretreatment with alkaline hydrogen peroxide and extrusion combined were highly effective in increasing hydration properties of rice hulls fiber

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